trifluoroacetonitrile was added. At the conclusion of the reaction, the system was purged with nitrogen and the solvent removed by distillation. The remaining liquid was transferred to a micro distillation apparatus and the final traces of solvent were removed at atmospheric pressure. The remaining liquid was then distilled under reduced pressure to yield the fractions shown in Table I.

TABLE I

Fraction	B.p., °C. (mm.)	Amount, g.
I	90	2.8
II	55–106 (92)	1.5
III	106–111 (92)	6.5
IV	100 (32)	2.0

Fractions I and II were solvent while III was the borazine which crystallized on cooling. Fraction IV was contaminated borazine and there remained an oily residue that slowly became viscous on cooling.

Anal. Calcd. for $(CF_3CH_2NBH)_3$: C, 22.10; H, 2.76; N, 12.90; F, 52.5; B, 9.98; mol. wt., 327. Found: C, 21.36; H, 2.20; N, 12.08; F, 53.67; B, 9.77; mol. wt. (boiling point elevation in benzene), 332. The material is slowly hydrolyzed by moisture although not soluble in water.

Anal. Found for residue: C, 19.11; H, 3.18; N, 9.72; B, 9.89. The material slowly changed to a white powder on standing, indicating the formation of boric oxide. Not enough was available to determine decomposition products.

An attempt was made to determine the number of hydridic hydrogen atoms per unit structure of the residue by methanolysis in a sealed tube. A sample weighing 0.1272 g. was heated with excess methanol for 3 hr. on a steam bath and 0.45 mmole of hydrogen was evolved. If the basic structure is $(CF_3CHBNH)_n$, 1.17 mmoles of hydrogen would have been evolved, indicating either incomplete reaction or less hydridic hydrogen in the structure. A second sample weighing 0.1690 g. was pyrolyzed at 300° for 16 hr. and only 0.40 mmole of hydrogen was evolved. This also indicated less B–H bonding than theoretically expected.

Reaction of Trichloroacetonitrile and Diborane. (a) Vapor Phase.—The reactions were carried out in 500-ml. sealed bulbs equipped with breakers. In a typical reaction 1.1037 g. (7.65 mmoles) of trichloroacetonitrile and 3.22 mmoles of diborane were mixed at room temperature with no noticeable reaction and then heated to 85° for 15 hr. After cooling, crystals were deposited over the surface of the bulb. The bulb was opened to the vacuum system and 0.38 mmole of noncondensable gas was measured plus 0.10 mmole of unreacted diborane, giving a reaction ratio of trichloroacetonitrile to diborane of 2.38. Other runs gave ratios of 2.38 to 2.75 and in some cases a liquid was also present that reacted rapidly with methanol. Sublimation of the solid product at 130° under vacuum yielded a crystalline white powder, m.p. 202–203°.

Anal. Calcd. for $(CCl_3CH_2NBH)_3$: C, 15.15; H, 1.89; N, 8.85; Cl, 67.30; B, 6.85; mol. wt., 478. Found: C, 15.21; H, 2.01; N, 8.61; Cl, 67.16; B, 7.00; mol. wt., 477.

(b) In Dimethoxyethane.—In a 500 ml. three-necked flask fitted with gas inlet tube, stirrer, and condenser was placed 57 g. (0.392 mole) of trichloroacetonitrile and 200 ml. of dimethoxyethane. The flask was purged with dry nitrogen and diborane was added at a rate of 30 ml./min. until a calculated excess was present. The system was again purged with nitrogen and the solvent was removed under water aspirator vacuum. The remaining slurry was washed with 30–60° petroleum ether to remove the last traces of ether and to leave a fine powder (38 g.). This material, m.p. 116°, could be sublimed at 110–120° under vacuum and was the intermediate, $CCl_3CH{:}NBH_2$.

Anal. Calcd. for $CCl_3CH{:}NBH_2$: C, 15.15; H, 1.89; N, 8.85; Cl, 67.30; B, 6.85. Found: C, 15.00; H, 1.87; N, 8.61; Cl, 67.03; B, 6.55.

In order to determine the number of hydridic hydrogens per molecule a freshly prepared sample of intermediate was treated with methanol and the hydrogen measured. A sample of 0.1735 g. (1.20 mmoles) of trichloroacetonitrile in 5 ml. of dimethoxyethane was allowed to react with 1.625 mmoles of diborane in a 50-ml. flask attached to the vacuum system. After the reaction was complete all of the volatile materials were removed by pumping and excess methanol condensed onto the product. This yielded 2.275 mmoles of hydrogen as measured in the Toepler pump giving a H_2/CCl_3CN ratio of 1.895, establishing the presence of two hydridic atoms per molecule.

The intermediate was conveniently converted into the borazine by heating in an inert solvent. A sample of 20.9 g. of intermediate was suspended in mineral spirits at 140° for 2 hr., the mixture was cooled, and the product was filtered off to yield 11.4 g. (54.5%). Several explosions resulted from heating the dry intermediate.

Reaction of N,N′,N″-Tris(β,β,β-trichloroethyl)borazine with Antimony Trifluoride.—A mixture of 4 g. of the borazine and 12 g. of antimony trifluoride was suspended in 30 ml. of toluene and heated to 110° for 3 hr. The mixture was cooled to room temperature and the antimony salt filtered off. Evaporation of the toluene left the unreacted starting borazine.

Reaction of N,N′,N″-Tris(β,β,β-trichloroethyl)borazine with Phenylmagnesium Bromide.—A solution of phenylmagnesium bromide was prepared in a 500-ml. three-necked flask equipped with a stirrer, condenser, and addition funnel by treating 3.3 g. of magnesium with 14 ml. of bromobenzene in 150 ml. of anhydrous diethyl ether in a nitrogen atmosphere. To this was added 4 g. of the solid borazine in small amounts and the mixture was allowed to stir overnight. The resultant product was hydrolyzed, hydrochloric acid was added to dissolve the magnesium hydroxide, and the ether solution was separated. It was washed with water, the ether was evaporated, and the residue was crystallized from carbon tetrachloride. The product was a light tan solid, m.p. 228–230°, and was identified as triphenylboroxine.

Anal. Calcd. for $(C_6H_5BO)_3$: C, 69.4; H, 4.82; B, 10.35; mol. wt., 311.4. Found: C, 68.63; H, 4.75; B, 10.61; N, 0.35; Cl, 0.45; mol. wt., 319.5.

Reaction of β,β,β-Trifluoroethylamine and Diborane.—Trifluoroethylamine was prepared from trifluoroacetic acid by known methods.[4] The amine–borane adduct was formed from 10 g. of the amine and 1.5 l. (STP) of diborane in diethyl ether. The ether was evaporated and the adduct held at 140° overnight in a long tube in a nitrogen atmosphere. The residue was sublimed *in vacuo* to yield the borazine, m.p. 40–41°.

Anal. Calcd. for $(CF_3CH_2NBH)_3$: N, 12.90; B, 9.98. Found: N, 12.70; B, 9.30.

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[4] E. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1256 (1959).

CONTRIBUTION FROM THE NATIONAL LEAD COMPANY
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Crystalline Hydrous Zirconia

BY A. CLEARFIELD

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X-Ray diffraction studies[1,2] have shown that the zirconyl ion in the zirconyl halides is a tetramer, $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}$, and that this species also exists in aqueous solution. Addition of base to zirconyl halide solutions results in further polymerization and eventual precipitation of a gelatinous, amorphous,

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[1] A. Clearfield and P. A. Vaughan, *Acta Cryst.*, **9**, 555 (1956).

[2] G. M. Muha and P. A. Vaughan, *J. Chem. Phys.*, **33**, 194 (1960).

hydrous oxide.[3,4] Heating or otherwise aging the solutions also brings about polymerization.[3]

Lundgren[5] pointed out that there is a similarity in structure between cubic ZrO_2 and the tetrameric species of the zirconyl halides. This observation is of value in developing a mechanism for the hydrolytic polymerization if some connection between the structure of the actual hydrolysis product, hydrous zirconia, and either ZrO_2 or the tetrameric species can be shown. However, little is known about the structure of hydrous zirconia because of its amorphous character. Previous attempts to induce crystallinity have only been partially successful.[6] It has now been found that crystalline forms of hydrous zirconia related in structure to the calcined oxides can be prepared under special conditions.

Experimental

Reagents.—Zirconyl chloride was recrystallized from hydrochloric acid until spectrographically pure. A stock solution, 1 *M* in Zr, was prepared from distilled, de-ionized water and used for all the experimental work. All pH measurements were taken with a Beckman Model G pH meter and glass electrode.

Preparation of Monoclinic Hydrous Zirconia.—Portions of the 1 *M* zirconyl chloride stock solution were adjusted to pH values between 1 and 2.5 by addition of ammonia. A small amount of precipitate formed which redissolved on heating. The clear solutions were then refluxed and samples removed at various time intervals. The samples were cooled to room temperature and their pH recorded. The pH of the solutions was found to decrease continuously with refluxing as shown by the following typical example.

Time, hr.	0	1	3	19	26	44
pH	2.5	1.6	1.1	0.9	0.7	0.4

Precipitation usually began in about 20 hr. and continued for many hours thereafter. The final product was a colloidal sol. The solid particles were collected by centrifugation or by coagulation with ammonia. The air-dried solid gave an X-ray diffraction pattern characteristic of monoclinic zirconia. During the early stages of the precipitation the X-ray patterns also contained evidence for the presence of some cubic zirconia.

Crystalline products were also prepared by refluxing slurries of hydrous zirconia. Gelatinous, amorphous hydrous zirconia was precipitated by addition of ammonia to the zirconyl chloride stock solution. The thoroughly washed, filtered gels contained 18–20% ZrO_2 and 0.1–0.4% Cl^-. The amount of chloride ion retained by the gel was greater the lower the final pH at which it was precipitated, in accord with previous observations.[7] Slurries were prepared from equal weights of gel and distilled, de-ionized water.

The rate of decrease in pH of the slurries and the time required for crystallinity to develop were much slower than previously noted for zirconyl chloride solutions. During refluxing the chloride ions present in the solid phase migrated into the aqueous phase, having presumably been displaced by hydroxyl ions.[8] If the chloride ion was first completely removed from the hydrous zirconia by washing with dilute ammonia followed by extensive water washing, no pH decrease occurred and no crystallinity developed.

Initially, the crystalline products obtained from the refluxed slurries consisted of a mixture of cubic and monoclinic zirconia. However, as the slurries were further refluxed the proportion of cubic zirconia in the products decreased and finally only monoclinic zirconia was obtained.

Preparation of Cubic Hydrous Zirconia.—Cubic hydrous zirconia, free of the monoclinic phase, was prepared by heating amorphous hydrous zirconia in the presence of aqueous NaOH or KOH solutions. In a typical experiment 50 g. of hydrous zirconia was added to 200 ml. of 20% NaOH. The mixture was stirred until uniform and then boiled for 1 hr. The solid was then filtered off and washed until the pH of the wash water was approximately 12. The solid was then dried at 60–70°, reground, and washed until the pH of the wash water was neutral. The products still contained about 0.1% Na and also 0.2–0.5% SiO_2 on a calcined basis.

The cubic hydrous zirconia was found to be stable to 650°. Above this temperature it reverted to monoclinic zirconia. When the hydrous zirconia was not completely converted to cubic crystals by treatment with alkali, the uncrystallized portion formed monoclinic zirconia on calcination at 450–650°. By comparison of the intensities of their (111) X-ray reflections it was possible to obtain a rough estimate of the relative proportion of each phase in the calcined (450–650°) product. This permitted an approximate determination of the rate at which amorphous hydrous zirconia was converted to the cubic form under varied experimental conditions. The rate was observed to increase with increasing temperature and alkali concentration. Since these are just the conditions which increase the solubility of amorphous hydrous zirconia,[9] the reaction appears to involve crystallization from solution.

Discussion

The decrease in pH of partially neutralized zirconyl chloride solutions and the ensuing precipitation of hydrous zirconia indicate that extensive hydrolytic polymerization occurs on refluxing. X-Ray line broadening measurements show that the crystallites are initially 20–25 Å. in the [111] direction. This is equivalent to 12–24 unit cells of ZrO_2 or 48–96 monomer units and may well represent the upper limit of the size of the polymers obtained in solution.

Continued refluxing results in further crystal growth and crystallites as large as 120 Å. have been obtained. The interplanar spacings of these well formed crystallites are given in Table I together with the corresponding values for calcined ZrO_2 taken from the ASTM card index.[10]

TABLE I

INTERPLANAR SPACINGS OF CRYSTALLINE HYDROUS ZIRCONIA AND ZIRCONIUM DIOXIDE

Monoclinic		Cubic	
Hydrous	ZrO_2	Hydrous	ZrO_2
3.18	3.16	2.95	2.96
2.84	2.84	2.56	2.56
2.63	2.62	1.80	1.81
2.55	2.54	1.54	1.54
2.21	2.21		
2.02	2.02		
1.85	1.846		
1.82	1.817		

The close agreement between the interplanar spacings of the hydrous oxides and those of the calcined products indicates that within the crystallites the composition

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(8) A. W. Thomas and H. S. Owens, *J. Am. Chem. Soc.*, **57**, 1825 (1935).
(9) I. A. Sheka and Ts. V. Pevzner, *Russ. J. Inorg. Chem.*, **5**, 1119 (1960).
(10) A.S.T.M. X-Ray Powder Data File, Phila., Penna., 1955.

must be close to $[ZrO_2]_n$. However, the crystalline hydrous zirconias still contain significant amounts of coordinated water and hydroxyl groups as shown by their high ignition loss ($\sim$11% when dried over P_2O_5) and retention of ion-exchange properties.[11] These groups must be primarily located on the surface of the crystallites. Thus, the crystalline, hydrous zirconias are considered to be hydrated oxo-hydroxides.

The results reported here lend substance to Lundgren's observation. In a subsequent publication the structure of the various forms of hydrous zirconia will be discussed in more detail and their relationship to the aqueous Zr(IV) species developed.

(11) C. B. Amphlett, L. A. McDonald, and M. J. Redman, *J. Inorg. Nucl. Chem.*, **6**, 236 (1958).

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Molecular Addition Compounds of Tin(IV) Chloride. III. Thermodynamic Data for 1:1 Addition Compound Formation[1]

BY JAAN LAANE AND THEODORE L. BROWN[2]

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In an earlier study of the equilibria existing between benzonitrile and tin(IV) chlorides, it was observed that the 1:1 addition compound is the principal complex species present in dilute benzene solution, although formation of a 1:2 addition compound, $SnCl_4B_2$, was found to occur to a measurable extent.[3] We wish to report here some further observations on benzonitrile–tin(IV) chloride complexes, as well as data relating to the interaction of tin(IV) chloride with a few oxygen donors. Equilibrium constants have been evaluated as a function of a temperature to permit calculation of the enthalpy and entropy of complex formation.

Experimental

The substances employed as donors were obtained commercially and purified by drying and distillation or sublimation before use. Reagent grade tin(IV) chloride was fractionated over mercury before use. Reagent grade benzene was dried using sodium wire. All operations in the preparation and handling of solutions were conducted in a drybox.

Measurements were carried out with a Beckman IR-7 spectrophotometer using cells with sodium chloride windows, 0.4-mm. path length. The temperature was controlled to within about 0.2° by placing the cells in a box fitted with sodium chloride windows. Air, pre-heated or pre-cooled as required, is passed into the chamber. The temperature in the chamber is controlled by a thermistor element which controls the operation of a heater in the incoming air stream. The procedures involved in the determination of the equilibrium constants are essentially the same as those described earlier. In the present work the interest is in evaluation of only K_{11}, since it was concluded that K_{12} could not easily be evaluated with sufficient accuracy to be of use in estimating an enthalpy for 1:2 compound formation. In the case of the nitriles the concentration conditions imposed by the extinction coefficient of the nitrile band are such that a significant quantity of 1:2 compound formation occurs. The iterative technique described previously[3] was therefore employed in calculating K_{11}.

Addition compound formation in the carbonyl donor systems was measured by observation of the infrared carbonyl absorption. The carbonyl absorption for complexed molecules is shifted to lower frequency; the frequency shift is sufficiently large (Table I) so that the correction for overlap with the free carbonyl absorption is small. The extinction coefficients for the carbonyl bands are much higher than for the nitriles, and it was possible to achieve conditions under which formation of the 1:2 complex is negligible. K_{11} for the carbonyl donor systems was calculated, therefore, from the expression

$$K_{11} = \frac{B_0 - B}{B(A_0 - B_0 + B)}$$

where A_0 and B_0 represent the initial concentrations of tin(IV) chloride and carbonyl compound, respectively, and B represents the equilibrium concentration of free carbonyl compound, as determined from the infrared measurement. Preliminary studies revealed that K_{12} is smaller than K_{11}; by employing excess tin(IV) chloride to minimize formation of the 1:2 adduct, essentially constant values were obtained for K_{11} under varying concentration conditions.

Results

The results of the measurements are given in Tables I and II, along with values of ΔH and ΔS calculated from the $1/T$ dependence of log K. Each value listed for K is the result of measurements on a number of solutions, in which both donor and acid concentrations are varied over a tenfold range. The standard deviations in the values of K_{11} are in all cases about 0.2 or less. The uncertainty in the values of ΔH are estimated from the log K *vs.* $1/T$ graphs and the standard deviations for the values of log K. The uncertainty in ΔS is due largely to the uncertainty in the value of ΔH.

TABLE I
CARBONYL FREQUENCY DATA IN CARBONYL–TIN(IV) CHLORIDE BENZENE SOLUTIONS

Donor	ν_{free}	$\nu_{complex}$	$\Delta\nu$
Diisobutyl ketone	1712	1642	70
9-Fluorenone	1720	1666	54
Ethyl pivalate	1728	1646	82

It is to be noted that although the values listed for K are in units of l./mole, the values of ΔS were calculated[4] using K in units of atm.$^{-1}$.

Discussion

A graph of ΔH *vs.* ΔS for the five benzene solution systems listed in Table II is shown in Fig. 1. Linear enthalpy–entropy relationships such as that in Fig. 1 have been discussed recently by Person.[5] It is interesting that a linear relationship does in fact hold for

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(1) Address correspondence regarding this note to T. L. Brown. This research was supported by a PHS research grant, A-3551, from the Institute of Arthritis and Metabolic Diseases.

(2) Alfred P. Sloan Foundation Fellow.

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